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A density functional theory investigation on the properties of supramolecular catalysts for photoinitiated electron collection

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Abstract

In this work we investigated by density functional theory (DFT)/time-dependent DFT (TDDFT) supramolecular complexes for photoinitiated electron collection, in particular $[\{(bpy)_2Ru(dpp)\}_2RhCl_2]^{5+}$ and related catalysts derived by variation of the ligand/metal. The electron collection in this class of catalysts enables hydrogen production or DNA cleavage, among other applications. Changes in excitation energies upon variation of the ligand/metal were mostly consistent with experiment, and within the expected TDDFT accuracy, thus enabling their use as the basis for further analysis. Indeed, the consistency observed between the predicted excitation energy and the bridging ligand's reduction potential can assist in catalyst design for electron collection. Calculated fragment orbital energies could explain, in part, changes in the propensity towards photocleavage of DNA.

Keywords: Mixed-metal supramolecular complex; density functional theory; time dependent density functional theory, electronic spectrum, electron transfer

1. Introduction

Supramolecular photocatalysts, e.g. the complex $([\{(bpy)_2Ru(dpp)\}_2RhCl_2]^{5+}$, which undergo a photochemical two-electron reduction, have been shown to catalyze hydrogen production by photoinitiated electron collection. This supramolecular complex, comprising of two subunits (related by C_2 symmetry), each of which consists of a light absorber, i.e. 2,2'-bipyridine (bpy), and a bridging ligand, i.e. 2,3-bis(2-pyridil)pyrazine (dpp), was shown to produce 8.2 μmol of H_2 in 4 hours catalytically when excited with visible light (470 nm) in an acetonitrile/water solution in the presence of dimethyaniline (DMA). Similar results were obtained for the bromide analog [1, 2]. Notably, intramolecular electron collection of this class of photocatalysts also enabled light-activated DNA cleavage [3, 4], as well as inhibition of cell growth, thus providing promise as a photodynamic therapy agent [5]. Modulation of electron collection can be achieved by changing the light absorber or bridging ligand of the supramolecular catalyst [6], substituting Ru(II) to Os(II) within the supramolecular complex framework [7], changing the propensity

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towards electron collection, e.g. Rh to Ir [8, 9], or in replacing Br by a Cl analog [10]. Significant improvement in hydrogen production for such supramolecular complex derivatives has not however been demonstrated, but progress is noted. For example, upon photolysis and addition of H_2O in the presence of DMA of the $[\{(phen)_2Ru(dpp)\}_2Ru(dpq)PtCl_2]^{6+}$ catalyst, production of 21 μmol of H_2 in 5 hours was achieved [11]. Variation of the propensity towards DNA cleavage was also noticeable, resulting from changes in the complex's framework.

At the same time, although progress in synthesis was achieved, prediction of the supramolecular complexes' properties to enable validated design for tunability of electron collection and to explain experimental trends is still lacking. Density functional theory (DFT) can provide insight into the electrochemical behavior, while linear response time-dependent DFT (TDDFT) [12] has become a useful tool in predicting photophysical parameters. In this work, computationally intensive calculations were carried out for selected supramolecular complexes of the general composition $[\{(\text{light acceptor, LA})_2,M,(\text{bridging ligand, BL})\}_2(\text{electron collector, EC})X_2]$, in accordance with the available experimental characterization. The following supramolecular complexes were considered. (LA=bpy, BL=dpp): **1** M=Ru, EC=Rh, X=Cl, **2** M=Os, EC=Rh, X=Cl, **3** M=Ru, EC=Ir, X=Cl, **4** M=Ru, EC=Rh, X=Br; **5** (LA=tpy (2,2':6',2"-terpyridine, BL=dpp), M=Ru, EC=Rh, X=Cl; **6** (LA=bpy, BL=bpm, 2,2'-bipyrimidine), M=Ru, EC=Rh, X=Cl. The calculated results established a basis for further exploration of photoinitiated electron collection characteristics in this class of catalysts.

2. Computational details

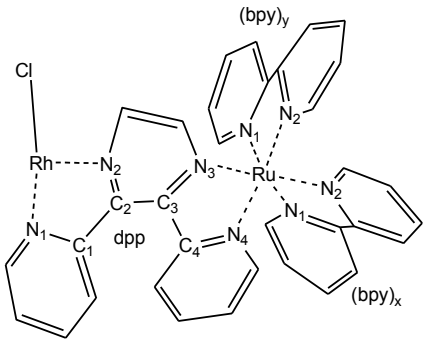
Geometries were optimized with the B3LYP [13] hybrid (x-c) functional, and for comparison also with PBE0, with a 6-31G(d)-LANL2DZ basis set and the LANL Effective Core Potential (ECP) [14]. A 6-311+G(3df,2p) basis set (3602 basis functions) was used for complex **1** for comparison. Changes in the optimized geometries when using either the B3LYP or PBE0 functional were small, as expected, shown by the bond lengths and bond angles for **1** [15]. Therefore, calculations are reported for B3LYP geometries. Note that no X-ray structure is available for this series of supramolecular complexes. Spectra were calculated by applying TDDFT with the B3LYP functional. B3LYP has been found adequate in previous work on Ru complexes [16, 17]. All calculations were performed using Gaussian 03 [18]. The line-shape was calculated as a sum of Gaussian bands with a full width half maximum value of 0.37 eV, using the software package SWizard [19].

3. Results and discussion

3.1. Structural parameters

A comparison of the geometrical parameters for supramolecular complexes **1**-**4** (see Table 1) demonstrated, for example, lengthening of the Rh-Br bond to 2.512 Å in **4**, as compared to 2.378 Å for Rh-Cl in **1**. The Ru-Rh bond was slightly lengthened in **4**, as compared to other derivatives, and variations in the metal-bridging ligand geometrical parameters were also noted. Lengthening of the bonds occurred when replacing Ru by Os (supramolecular complexes **1** vs. **2**). Furthermore, upon changing the bridging ligand dpp to bpm, the local geometry was modified accordingly, and bonds lengthened in **6** as compared to **1** [15]. Notably, in complex **6**, the structure of the bridging ligand (bpm) was almost co-planar, with a N1-C1-C2-N2 dihedral angle of about 2°, while a distortion from planarity is noted for **1** and N1-C1-C2-N2 of about 12° (similarly for **2**-**4**). The structure of dpp in a constrained supramolecular complex is known to deviate from that of the free ligand [20]. For supramolecular complexes **1**–**4** the deformation energies of dpp, estimated as the energy difference between the structure of the free ligand and of ligand within the complexes, ranged from 0.46 to 0.57 eV, with a 6-7° decrease in the 61° angle of the pyridine–pyridine plane in the free ligand.

Table 1: Geometries of optimized supramolecular complexes. Numbering for the C_2 related region is as follows:



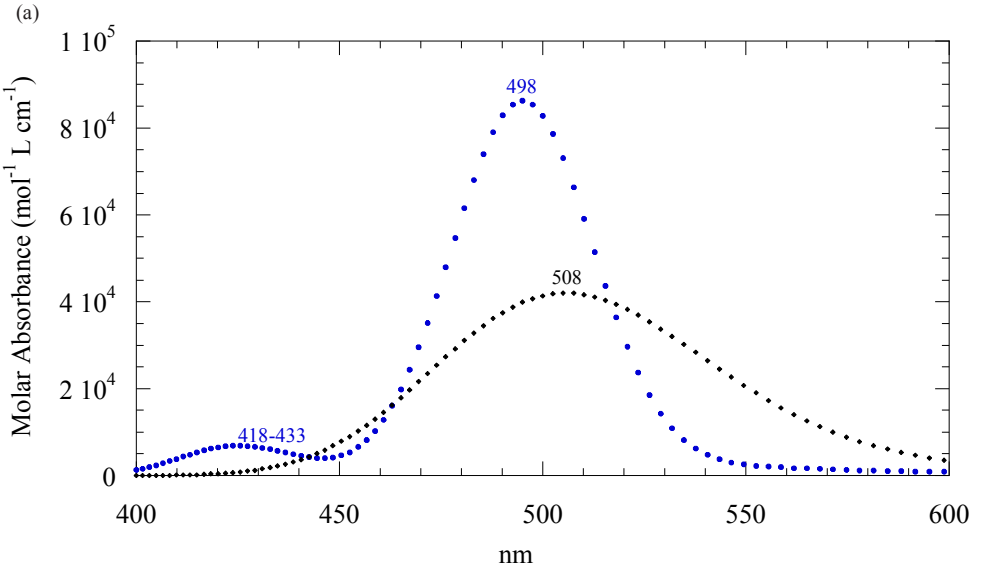
Bond length (Å)		Bond angle (º)	
$[\{(bpy)_2Ru(dpp)\}_2RhCl_2]^{5+}$			
Rh-Cl	2.378	Cl-Rh-N1 (dpp)	85.8
Rh-N1 (dpp)	2.106	Cl-Rh-N2 (dpp)	83.6
Rh-N2 (dpp)	2.082	N1-Rh-N2 (dpp)	77.7
Ru-N3 (dpp)	2.096	N3-Ru-N4 (dpp)	77.1
Ru-N4 (dpp)	2.115	N1-Ru-N2 $(bpy)_x$	77.4
Ru-N1 $(bpy)_x$	2.134	N1-Ru-N2 $(bpy)_y$	77.5
Ru-N2 $(bpy)_x$	2.122		
Ru-N1 $(bpy)_y$	2.131		
Ru-N2 $(bpy)_y$	2.123		
Ru-Ir	6.895		
$[\{(bpy)_2Ru(dpp)\}_2IrCl_2]^{5+}$			
Ir-Cl	2.401	Cl-Ir-N1 (dpp)	85.8
Ir-N1 (dpp)	2.080	Cl-Ir-N2 (dpp)	83.3
Ir-N2 (dpp)	2.070	N1-Ir-N2 (dpp)	77.8
Ru-N3 (dpp)	2.097	N3-Ru-N4 (dpp)	77.0
Ru-N4 (dpp)	2.115	N1-Ru-N2 $(bpy)_x$	77.4
Ru-N1 $(bpy)_x$	2.133	N1-Ru-N2 $(bpy)_y$	77.5
Ru-N2 $(bpy)_x$	2.123		
Ru-N1 $(bpy)_y$	2.131		
Ru-N2 $(bpy)_y$	2.123		
Ru-Ir	6.904		
$[[21]_2RhCl_2]^{5+}$			
Rh-Cl	2.379	Cl-Rh-N1 (dpp)	85.8
Rh-N1 (dpp)	2.105	Cl-Rh-N2 (dpp)	83.8
Rh-N2 (dpp)	2.080	N1-Rh-N2 (dpp)	77.6
Os-N3 (dpp)	2.043	N3-Os-N4 (dpp)	77.3
Os-N4 (dpp)	2.091	N1-Os-N2 $(bpy)_x$	76.9
Os-N1 $(bpy)_x$	2.120	N1-Os-N2 $(bpy)_y$	77.2
Os-N2 $(bpy)_x$	2.125		
Os-N1 $(bpy)_y$	2.111		
Os-N2 $(bpy)_y$	2.115		
Os-Rh	6.867		
$[\{(bpy)_2Ru(dpp)\}_2\ RhBr_2]^{5+}$			
Rh-Br	2.512	Br-Rh-N1 (dpp)	86.2
Rh-N1 (dpp)	2.122	Br-Rh-N2 (dpp)	83.6
Rh-N2 (dpp)	2.091	N1-Rh-N2 (dpp)	77.3
Ru-N3 (dpp)	2.095	N3-Ru-N4 (dpp)	77.0
Ru-N4 (dpp)	2.115	N1-Ru-N2 $(bpy)_x$	77.4
Ru-N1 $(bpy)_x$	2.133	N1-Ru-N2 $(bpy)_y$	77.4
Ru-N2 $(bpy)_x$	2.123		
Ru-N1 $(bpy)_y$	2.123		
Ru-N2 $(bpy)_y$	2.131		
Ru-Rh	6.919		

3.2. Excitation energies

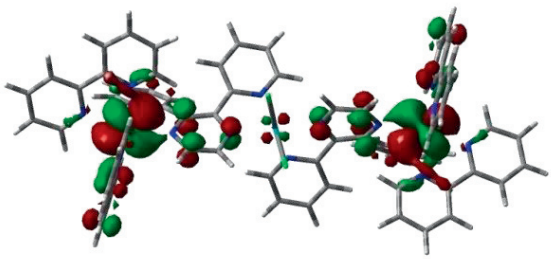
The calculated absorption spectrum of **1** at the B3LYP/6-31G(d)-LANL2DZ level is shown in Fig. 1(a) [15]. λ_{max} for **1** (2.49 eV) compares relatively well with the experimental value of 2.38 eV taken in solution, and within the expected range of TDDFT accuracy [21]. PBE0 resulted in an overestimation of the excitation energy (λ_{max} 2.65 eV). The importance of using range-separated hybrid functionals was recently emphasized [22], but this is not within the scope of this study. An improvement was obtained by increasing the basis set to 6-311+G(3df,2p), with an excitation energy of 2.4 eV (compared to 2.5 eV), also demonstrating an overlap of two transitions [15], which could explain the broad spectrum observed in the experimental data.

Selected frontier molecular orbitals (FMOs) for **1** involved in the transition with the largest oscillator strength are shown in Fig. 1(b), validating the role of the absorbing and bridging ligands in the supramolecular complex. Note that upon optimizing the **1** supramolecular structure with $(PF6)^-$ counter ions at the B3LYP/6-31G(d)-LANL2DZ level (shown in Fig. 2), in order to assess, in part, effects of the environment, the absorption maximum red-shifted to 2.45 eV, as compared to the value of 2.49 eV. Agreement with experiment improved by about 0.1 eV, but having broad absorption characteristics rules out a more careful comparison. The relatively good agreement with experiment overall enabled comparison among variants in the series of the supramolecular complexes.

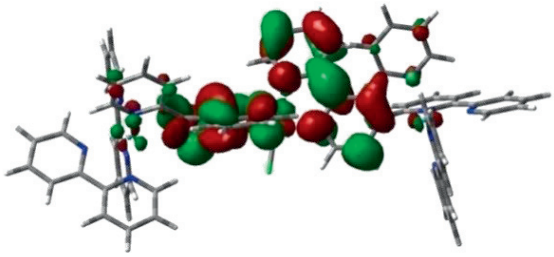
The supramolecular complex $[\{(bpy)_2Os(dpp)\}_2RhCl_2]^{5+}$ (**2**) showed a larger oscillator strength, of 0.63 [15], as compared to a value of 0.48 for **1**, which is consistent with experimental data [4]. Calculated spectra are similar for the supramolecular complexes **1** and **4** (Br substitution), resulting in maxima at 4.94 eV and 4.95 eV [15], also consistent with the experimentally measured λ_{max} for the two supramolecular complexes, of about 4.38 eV [4]. It was also shown experimentally that the spectra of **1** and **3** are very similar [3], as we have predicted. Modification of the LA from bpy to tpy (**5**) has caused a red-shift in the measured spectrum (2.38 eV to 2.30 eV) [4]. The computed results were only slightly red-shifted from 2.49 eV to 2.47 eV, however subject to improved agreement with a larger basis set, as mentioned. The relevant FMOs for the assigned transitions in this case, similar to complex **1** [15], are not predicted to impact electron collection significantly.



(b)



HOMO-5



LUMO

Fig. 1: (a) Absorption spectrum of **1**: blue line: B3LYP/6-31G(d)-LANL2DZ level; black line: 6-311+G(3df,2p)-DGDZVP level; (b) FMOs for **1** with 6-311+G(3df,2p) basis set.

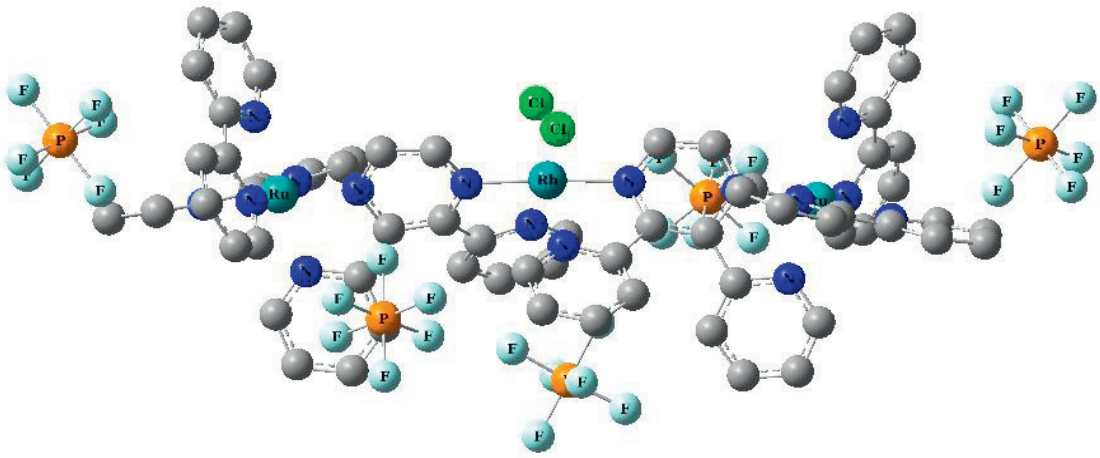


Fig. 2: Supramolecular optimized structure of supramolecular complex **1**, i.e. $[\{(bpy)_2Ru(dpp)\}_2RhCl_2]^{5+}$, with $(PF_6)^-$ counter ions.

3.3. Electrochemical properties

Interestingly, the similar excitation energies of complexes **1** and **3** are consistent with the similar reduction potentials for dpp for the two derivatives, as qualitatively expected [20]. For comparison, calculations for **1** were also performed where dpp was replaced by dpq (**7**) and dpb (**8**). The red-shift in the excitation energies of **7** and **8** of 0.28 and 0.25 eV as compared to **1**, respectively, is in agreement with the results for related compounds reported by Seneviratne et al. [20]. Upon changing to the bpm bridging ligand in **6**, a red-shifted absorption was observed, reproduced in our calculations yet underestimated, resulting in values of 1.92 eV and 2.50 eV, as compared to the experimental absorption maxima of 2.09 eV (a broad absorption lineshape noted), and 3.01 eV, respectively. Notably, a smaller reduction potential was measured for **6**, consistent with a correlation between the lowest energy metal-to-ligand charge transfer excitation and the reduction potential of the complex's bridging ligand. The results explain the observation that there is no evidence for hydrogen production for supramolecular complex **6**.

The character of the ligands strongly affects the electrochemical activity. As mentioned, modification of the bridging ligand from dpp to bpm demonstrated inactivity of **6** towards DNA cleavage, namely inhibition of electron collection, as compared to **1**. Superexchange electron transfer [23] that depends on the energy gap between the metal orbital and the bridging ligand's LUMO can explain the experimental observation, although subject to characterization of the photoinduced dynamics of the supramolecular complex. It is easier to reduce bpm according to the fragment orbital energies. Calculated fragment orbital energies, namely the PDOS' (partial density of states) contribution to the total DOS (T(otal)DOS), as summarized in Fig. 3, showed that the bpm orbital energy of -13.8 eV is lower than the value of -12.6 eV for dpp. Similarly, in substituting Rh to Ir, no DNA cleavage was observed because of the higher orbital energy [8,9]. In comparing **1** and **3**, the Ir orbital energy was -10.6 eV, vs. -11.7 eV for Rh, and the corresponding values for dpp were, respectively, largely consistent with experiment [3]. Although a slight discrepancy is noted for **1**, it could be improved upon by using a larger basis set, as the difference between the orbital energies of the fragments, for example the LUMOs of dpp and Rh decreased.

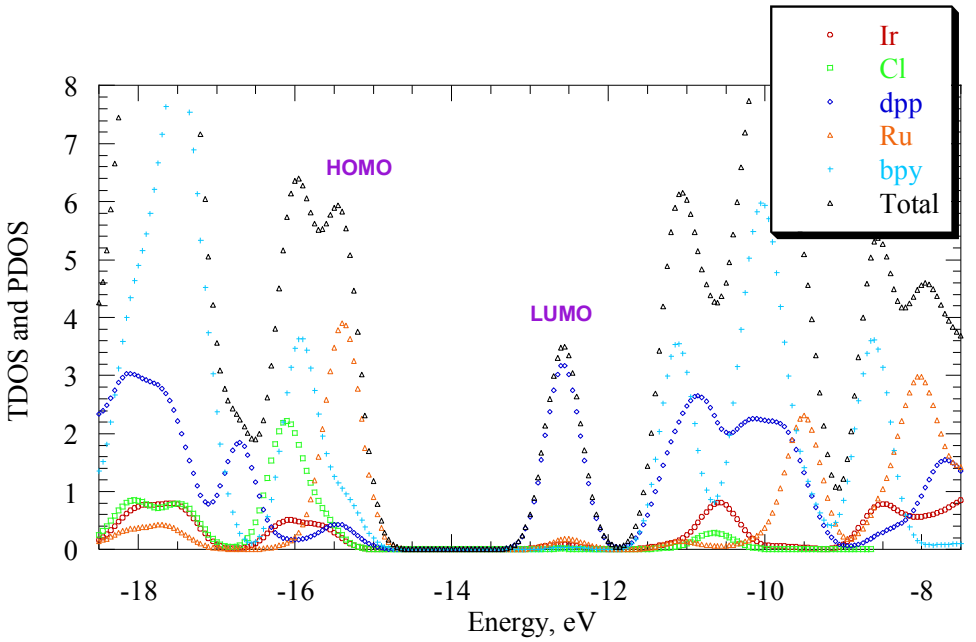


Fig. 3: TDOS and PDOS for complex **3**.

4. Conclusion

In this work we reported on properties of a series of supramolecular complexes that were developed for photoinitiated electron collection applications. Changes in the calculated absorption spectra upon variation of the ligand/metal in the [{(light acceptor, $LA)_2$,M,(bridging ligand, $BL)\}_2$(electron collector, $EC)X_2]^{5+}$ catalyst's framework were mostly consistent with experiment, and within the expected TDDFT accuracy. Improvement in prediction of the experimental data was shown to be expected upon careful inclusion of environmental effects and use of larger basis sets. Insight into aspects of the electrochemical properties was obtained by fragment analyses of the FMOs. Changes in the orbital energies could explain, in part, the change in photocleavage of DNA. The consistency observed between the excitation energies and the bridging ligand's reduction potential can assist in future catalyst design. However, for design of improved catalysts for hydrogen production that are based on electron collection in a supramolecular framework [24], more pronounced variations of the basic building blocks will be necessary.

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